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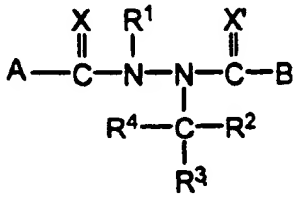
(54) Title: INSECTICIDAL COMPOSITION

(57) Abstract

A method of mothproofing wool or a wool-containing product, the method including treating the wool or wool-containing product with an effective amount of a compound according to formula (I).



(I)

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INSECTICIDAL COMPOSITION

Technical Field

The present invention is concerned with the use of insecticidally active compounds for the treatment of wool or wool-containing materials. The invention is also concerned with insecticidally active compositions which are capable of protecting wool or wool-containing materials against insect attack.

Background

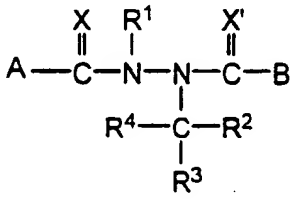
Permethrin is currently the main commercial mothproofing chemical. In the UK, aquatic discharges of permethrin will be restricted from the start of 1993. This decision effectively stops the dyebath application of permethrin, as small amounts of insect resist chemical will always be discharged with the exhausted liquors even under the best industrial conditions. Although permethrin can still be used for treatment of wool, it must be applied in totally contained systems that do not give rise to environmental residues.

The suitability of permethrin for insect-resist treatment of wool in Australia has declined due to the occurrence of a pyrethroid-resistant strain of the case bearing clothes moth (*Tinea translucens*) Increased application levels of permethrin have been used as a temporary measure to combat this insect, but this has exacerbated the environmental problems by increasing dyebath discharges.

Dyebath application is the simplest, cheapest and most universal point in the wool processing sequence to apply mothproofing agents; no specialised equipment is needed, and the high temperature application provides a treatment with optimum fastness properties. If insect-resist agents are to be applied to wool in the dyebath, special compounds with very low hazard to aquatic organisms of all kinds must be used.

Disclosure of the Invention

It is an object of the present invention to provide an insecticidally active composition and method of treatment which can be used to provide practical mothproofing for wool or wool product such as textiles. A further object of this invention is to provide a mothproofing treatment which is more environmentally acceptable that the prior art treatments referred to above. We have found that the insecticidally active N-optionally substituted-N'-substituted hydrazines of formula (I) below as disclosed in Australian Patent application no. 76287/87 (the disclosure of which is incorporated herein by reference) may be used to provide an effective mothproofing treatment of wool or wool-containing products.



(I)

where the substituents A, B, X, X', R^1, R^2, R^3 and R^4 are as defined in above-mentioned Australian application no. 76287/87, that is, wherein X and X' are the same or different O,S or NR;

R^1 is hydrogen; (C_1-C_6) alkyl; (C_1-C_6) alkoxy-(C_1-C_6) alkoxy-(C_1-C_6) alkyl having independently the stated number of carbon atoms in each alkyl group; (C_1-C_6) alkylthio-(C-C_6) alkyl having independently the stated number of carbon atoms in each alkyl group; (C_2-C_6) alkenyl; (C_2-C_6) alkynyl; or phen-(C_1-C_4) alkyl where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo-(C_1-C_4) alkyl (C_1-C_4)-alkoxy, halo-(C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy- carbonyl, (C_1-C_4) alkanoyloxy or NZZ';

R^2 and R^3 are the same or different hydrogen or (C_1-C_4) alkyl;

R^4 is (C_1-C_4) alkyl substituted with 1 to 4 fluoro; straight chain (C_2-C_4) alkenyl; carboxyl; (C_1-C_3) alkoxy-carbonyl; cyano; cyano substituted (C_1-C_4) alkyl, tri(C_1-C_4)-alkysilyl having independently the stated number of carbon atoms in each alkyl group; or tri(C_1-C_2) alkylsilylmethyl having independently the stated number of carbon atoms in each alkyl group; provided that R^2 and R^3 are both alkyl when R^4 is carboxyl or alkoxycarbonyl; and

A and B are the same or different unsubstituted or substituted naphthytyl where the substituents can be from one to three of the same or different halo; nitro; (C_1-C_4)-alkoxy; (C_1-C_4) alkyl or NZZ';

unsubstituted or substituted phenyl where the substituents can be from one to five of the same or different halo; nitroso; nitro; cyano; hydroxy; (C_1-C_6) alkyl; halo-(C_1-C_6)-alkyl; cyano-(C_1-C_6) alkyl; hydroxy-(C_1-C_6)-alkyl; (C_1-C_6)alkoxy; halo-(C_1-C_6) alkoxy; (C_1-C_6) alkoxy-(C_1-C_6) alkyl having independently the stated number of carbon atoms in each alkyl group; (C_1-C_6) alkoxy-(C_1-C_6) alkoxy having independently the stated number of carbon atoms in each alkyl group; -ORSR' group; -OCO_2R group; -OCO_2H group; (C_1-$_6$) alkanoyloxy-(C_1-C_6) alkyl having independently the stated number of carbon atoms in each alkyl group; (C_2-C_6) alkenyl optionally substituted with halo, cyano, (C_1-C_4) alkyl, halo-(C_1-C_4)-alkoxy, (C_1-C_4) alkylthio or (C_1-C_4)alkoxy; (C_1-C_4)alkadienyl; (C_2-C_6) alkenyloxy; (C_2-C_6) alkenyl-carbonyl; (C_2C_6)-alkenyloxy-carbonyloxy; (C_2-C_6) alkynyl optionally substituted with halo, cyano, nitro, hydroxy, (C_1-C_4) alkoxy, halo-(C_1-C_4)alkyl, (C_1-C_4) alkylthio or (C_1-C_4)-alkyl; carboxy; -RCO_2R' group; -COR; -COH; halo-(C_1-C_6) alkyl-carbonyl; -CO_2R group; (C_1-C_6) haloalkoxy-carbonyl; -OCOR group; -$ORCO_2$R' group; amino (-NZZ'); amino substituted with hydroxy, (C_1-C_4) alkoxy or (C_1-C_4) alkylthio; -CONZZ' group; (C_2-C_6)- alkenyl-carbonylamino; hydroxy-(C_1-C_6)-alkylamino-carbonyl; -OCONZZ' group; -NZCOZ' group; -$NZCO_2$Z' group; thiocyanato; isothiocyanato; (C_1-C_6) thiocyanatoalkyl; (C_1-C_6) alkylthio; halo-(C_1-C_6) alkylthio; -S(O)Z group; -SO_2Z group; -OSO_2R group; -OSO_2H group; -SO_2NZZ' group; -CSR group; -CSH group; -SCOR group; -SCOH group -NSCSZ' group; unsubstituted or substituted phenyl having one to three of the same or different halo, cyano, nitro, hydroxy (C_1-C_4) alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, amino, (C_1-C_4)-alkylamino or di(C_1-C_4) alkylamino having independently

the stated number of carbon atoms in each alkyl group; phenoxy where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo-(C_1-C_4) alkyl, (C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkyl-carbonyl, (C_1-C_4)alkanoyloxy, amino, (C_1-C_4)-alkylamino or di(C_1-C_4)alkylamino having independently the stated number of carbon atoms in each alkyl group; benzoyl where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, amino, (C_1-C_4) alkylamino or di(C_1-C_4)alkylamino having independently the stated number of carbon atoms in each alkyl group; benzoyloxy (C_1-C_6)alkyl; phenylthio-(C_1-C_6) alkyl where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy,(C_1-C_4) alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1.C_4)-alkanoyloxy, amino, (C_1-C_4)alkylamino or di(C_1-C_4)alkylamino having independently the stated number of carbon atoms in each alkyl group; -CR=N-R'" group where R'" is hydroxy, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, amino (-NZZ'), phenylamino, -COR, -COH or benzoyl; (C_2-c_6) oxiranyl; acetylthiosemi- carbazone; pyrrolyl; oxazolyl, unsubstituted or substituted with one or two methyl group; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups may be joined to form, together with the carbon atoms to which they are attached, a 5 or 6 membered dioxolano or dioxano heterocyclic ring; unsubstituted or substituted (C_1-C_{10})alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkoxy, halo-(C_1-C_4)alkoxy, carboxy, (C_1C_4)-alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, phenyl or -NZZ';

unsubstituted or substituted (C_3-C_8) cycloalkyl or unsubstituted or substituted (C_3-C_8) cyclo (C_1-C_4) alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alyl, halo-(C_1-C_4)-alkyl, (C_1-C_4) alkoxy, halo-(C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkanoyl, (C_1-C_4)-alkoxy-carbonyl, (C_1-C_4) alkanoyloxy or -NZZ';

unsubstituted or substituted (C_2-C_8)alkenyl or unsubstituted or substituted (C_2-C_8)-alkadienyl having as substituent(s) a furyl, thienyl or pyridyl or one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, (C_3-C_6)cycloalkyl, halo-(C_1-

C_4)alkyl, (C_1-C_4)alkoxy, halo-(C_1-C_4)alkoxy, carboxy, (C_1-C_4)-alkoxyl-carbonyl, (C_1-C_4) alkanoyloxy or -NZZ';

unsubstituted or substituted (C_3-C_8)cycloalkenyl or unsubstituted or substituted (C_3-C_8)cycloalkadienyl having as substituent(s) one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)-alkoxy, halo-(C_1-C_4)alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy or -NZZ';

unsubstituted or substituted (C_2-C_8)alkynyl having as substituent(s) one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-(C_1-C_4)alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, phenyl or -NZZ';

phenalkyl having one to four carbon atoms in the alkyl group and wherein the alkyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C_1-C_4)alkoxy, (C_1-C_4)-alkoxy-carbonyl or -NZZ' and the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, halo-(C_1-C_4)alkyl, cyano-(C_1-C_4)alkyl, (C_1-C_4)-alkoxy, halo-(C_1-C_4) alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, (C_2-C_6)alkenyl, halo-(C_2-C_6)alkenyl, (C_2-C_6)alkynyl or -NZZ';

phenalkenyl having two to six carbon atoms in the alkenyl group and the alkenyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C_1-C_4)alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-(C_1-C_4)alkoxy, (C_1-C_4)-alkoxy-carbonyl or -NZZ', and the phenyl ring is unsubstituted or substituted with one to or three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-(C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy or -NZZ';

unsubstituted or substituted five-membered heterocycle selected from furyl, thienyl, triazolyl, pyrrolyl, isopyrrolyl, pyrazolyl, isoimdazolyl, thizolyl, isothiazolyl, oxazolyl and isooxazolyl where the substituents can be from one to three of the same or different halo; nitro; hydroxy; (C_1-C_6)alkyl; (C_1-C_6)alkoxy; carboxy; (C_1-C_6) alkoxy-carbonyl; -RCO_2H group RCO_2R' group; -CONZZ' group; amino (-NZZ'); -NZCOZ' group; (C_1-C_6)alkylthio; or unsubstituted or halo substituted phenyl having one to three of the same or differnt halo, nitro, (C_1-C_6)alkyl, halo-alkyl, (C_1-C_6)alkoxy, halo- (C_1-C_6)-alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl or amino (-NZZ'); or

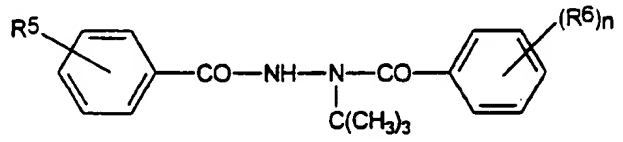
unsubstituted or substituted six-membered heterocycle having one, two, three or four nitrogen atoms and two to five nuclear carbon atoms where the substituents can be from one to three of the same or different halo; nitro; hydroxy; (C_1-C_6)alkyl; (C_1-C_6)alkoxy; carboxy; (C_1-C_6)-alkoxy-carbonyl; -RCO_2H group; -RCO_2R' group; -CONZZ' group; amino (-NZZ'); -NZCOZ' group; (C_1-C_6)alkylthio; or unsubstituted or substituted phenyl having one to three of the same or different halo, nitro, (C_1-C_6)alkyl, halo-(C_1-C_6)alkyl, (C_1-C_6) alkyl, (C_1-C_6)alkoxy, halo-(C_1-C_6)- alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl or amino (-NZZ');

where R and R' are (C_1-C_6)alkyl; Z and Z' are hydrogen or (C_1-C_4)alkyl; "amino" means NZZ'.

Accordingly, the present invention provides a method of mothproofing wool or a wool-containing product said method including treating said wool or wool-containing product with an effective amount of a compound according to the formula (I)

Preferably the treatment compound has relatively low water solubility. Preferably the water solubility of the treatment compound is less than 1 mg/l, although compounds with higher solubility may be used.

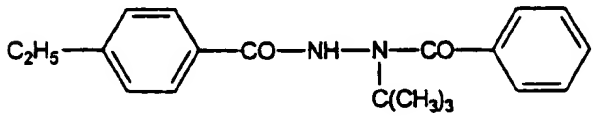
Preferably the treatment compound is a compound having the following formula:



(II)

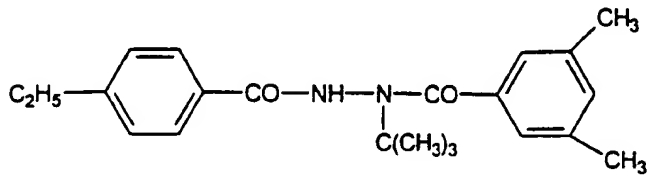
wherein R^5 and R^6 which may be identical or different may be selected from H or C_{1-3} alkyl and n=1-5.

The treatment compound may be of the formula:



(III)

Especially preferred is a compound of formula (IV) , the treatment compound has formula:



(IV)

The treatment compound may be applied at a level of about 0.001% - 0.5%.

The treatment compound may be applied in a dyebath, either to the whole of the wool or wool blend lot, or by overtreatment of a small fraction with subsequent blending with untreated wool. Alternatively the treatment compound may be applied by continuous padding, scouring application, continuous application in chemical setting or tape scouring, foam application, encapsulation in particles, centrifuge, or minibowl. The wool product may be subjected to steaming or heating following application of the treatment compound.

The treatment compound may be applied as a solution in an organic solvent, for example, ethanol. The treatment compound may also be applied as a suspension of the micro-ground compound, a self-emulsifiable concentrate or other water-based formulation as application vehicles.

Compound (IV), which is relatively hydrophobic, has a specific activity to lepidoptera larvae and with water solubility below 1mg/l, is more environmentally acceptable than permethrin. We have found that the treatment compounds of the present invention have very high insecticidal activity against all five of our test strains of clothes moths: common clothes moth (*Tineola bisselliella*), dieldrin resistant and dieldrin susceptible strains; casebearing clothes moth (*Tinea translucens*), susceptible, dieldrin resistant and pyrethroid resistant strain.

Insect-resist activity is required to persist through the life-time of a wool product. Application of 5-10 fold excess of active ingredient above the minimum active level may

be used to ensure protection even after 80%-90% losses through volatility, exposure to light, and cleaning (washing, shampooing and dry-cleaning).

We have found that compound (IV) has more than adequate fastness for a commercial insect-resist treatment. We have also found that compound (IV) has similar washing performance to conventional synthetic pyrethroid (permethrin or cycloprothrin) mothproofing compounds and better dry cleaning resistance and light fastness.

In insect-resist treatment of wool products, it is highly desirable to also provide protection against beetles such as a carpet beetle species. Compounds according to formula (I) do not have significant activity against beetles.

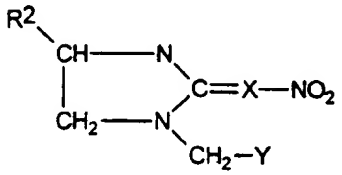
Accordingly, the present invention provides, in a second aspect, a method of treating a wool or wool-containing product the method including treating the wool or wool-containing product with a compound according to formula (I) together with an agent which has an activity against beetles.

It has been surprisingly found that the presence of a treatment compound of the invention may have a synergistic effect on the activity of an agent having activity against beetles.

The agent active against beetles may be a compound selected from synthetic pyrethroids, repellants and disinfectant materials, and other specialty wool insect resist agents of the aryl ureido and amide class.

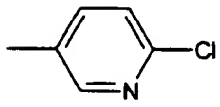
The agent active against beetles may be permethrin or bifenthrin, as examples of pyrethroids with a high activity against beetles. The agent may be selected from hexahydropyrimidine derivative (HHP): N-(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-6-hydroxy-1,3-dimethyl-2,4-dioxo-5-pyrimidinecarboxamide, flucofuron: N,N'-bis[4-chloro-3-(trifluoromethyl)phenyl] urea, butyl ester of 4-hydroxy benzoic acid, and sulcofuron:5-chloro-2-(4-chloro-2-(3,4-chlorophenyl)) phenoxyureido benzene sulfonate (as alkali salt, for example the sodium salt).

The agent having activity against beetles may be a nitromethylene of formula (V):



(V)

where R^2 is H or CH_3; X is CH or N; and Y is



Preferably the agent having activity against beetles is applied at a level of about 0.0001% to 0.1%.

In a further aspect the present invention provides a treatement composition suitable for use in the method of the present invention said composition including one or more compounds of formula (I) to (IV) and optionally including one or more compounds active against beetles.

In order that the invention may more readily be understood the following examples are provided. It will be clear to the reader that the invention is not limited to the particular exemplification provided hereunder.

Brief Description of the Drawings

The following description makes reference to the attached figures in which:

Figure 1 shows the Freundlich adsorption isotherm for compound (IV) on wool at 100°C, 30 min;

Figure 2 is a graph showing light fastness of woolen fabrics treated with compound (IV);

Figure 3 is a graph showing the handwashing characteristics of fabrics treated with compound (IV); and

Figure 4 is a graph showing the effect of dry cleaning on wool treated with compound (IV).

EXPERIMENTAL

Insect Bioassay

Compounds according to formula (III) may be prepared by benzoylation of a t-butyl hydrazine under Schotten-Baumann conditions. The product was recrystallised from methanol-ether; purity and structure were confirmed by nmr.

For initial bioassay, compounds were dissolved in ethanol at appropriate concentrations, then applied to prewetted, centrifuged wool fabric so as to evenly cover the fabric without run-off. Less than 2ml of ethanol was applied to 2g of fabric. Formulated Compound (IV) was also applied by aqueous dilution of water suspension formulation (Compound (IV) FL 20%ai). Samples were air dried before testing. Treatment levels between 0.1% and 0.0001% were used. Insect bioassay was according to AS2001 [1]. Minimum effective concentrations (MECs) were determined as the amount sufficient to inhibit larval feeding to less than 8mg damage when untreated voracity control fabrics showed at least 30 mg damage. Reported values are the means of at least two determinations.

Dyebath Application

Wool was treated with the insecticide in an Ahiba dyeing apparatus at 100°C for 30 minutes as described in AS2001. The insecticide was applied at the start of the dyeing cycle either as an ethanol solution, or as a micro-ground suspension (Compound (IV) 2F 23%ai or Compound (IV) FL 20%ai). Fabrics were rinsed in cold water then air dried after application. Generally 20g of wool was treated in 500cm^3 of water.

Chemical Analysis of Dyebath Liquors

Hot dyebath liquors (75ml) were taken from the dyebath and diluted to 100ml with methanol. The resulting solutions were used directly for HPLC analysis.

Wash and Dry Clean Fastness testing

Hand washing methods have been described previously [2]. Drycleaning was performed in commercial equipment using perchloroethylene solvent.

Light Stability Studies

Accelerated exposure to light was conducted in fan ventilated boxes equipped with 500W Phillips G-74 mercury-tungsten fluorescent lamps. A thermostatically controlled fan was used to maintain the black body temperature at 67°C [2].

Chemical Analysis of Fabrics

Fabric samples (0.2g) were extracted with a solution of methanol/water (75:25 v/v) (5ml) with shaking at 80°C. After the vessels were treated for an additional 30 min in an ultrasonic bath, the methanol/water solution was filtered and taken for HPLC analysis. Compound. (II) (where R_5 and R_6 are H) is used as an internal standard for analysis of Compound (IV).

HPLC Chemical Analysis

A Varian Star System HPLC fitted with a diode array detector and a variable wavelength detector usually set at 210 nm was used. Samples from dry-cleaning showed an interfering peak at 210nm and 265nm detection was used. A Brownlee Labs Spheri-5 RP8S (10cm length, 4.6mm ID) cartridge column was maintained at 40°C with an elution solvent of acetonitrile/water (57:43).

Insecticidal Activity against Moth and Beetle Species

Compound in accordance with formula (I) have very high insecticidal activity against all five of our strains of clothes moths, but as expected, there was very weak beetle activity at the highest levels tested. However as indicated above, if beetle protection is also

needed, the compounds of formula (I) will need to be used in a mixture with a compound active against carpet beetles to guarantee protection to wool goods.

TABLE 1 Minimum Effective Concentrations of Compounds (% of active compound by weight on wool).

	Test Insect		
Compound	*Tineola**	*Tinea**	*Anthrenus Flavipes*
Compd. (III)	0.001		>0.1
Cmpd. (IV) (FL formulation)	0.005	0.001	>0.1
Cmpd. (IV) (ethanol)	0.001	0.0025	>0.1
Permethrin**	0.004	0.002	0.008

* Similar results were obtained with wild strains (dieldrin-resistant) and susceptible strains of common clothes moth (*Tineola bisselliella*) and case-bearing clothes moths (*Tinea translucens*).

** Permethrin was applied to wool from boiling dyebaths.

At application levels above 0.005%, the treatment compounds caused 100% kill in the 14 day test. At levels around 0.00025%, approximately 50% of the larvae were still alive, but appeared abnormal. Even at levels of 0.0001%, larval feeding was only 30-40% of control wool. At high level (0.1%), the *Tinea* larvae crawled from their cases before dying, usually an indicator of distress.

To ensure that an active residue of insecticide remains to compensate for losses during application and use over the life time of the wool goods, levels of active ingredient higher than these minimum effective levels will need to be applied.

Dyebath exhaustion

Chemical assay of liquors and fabrics (Table 2) indicated there were significant losses in the dyebath during application. Losses of Compound (III) were high, and appear related to the hgih water solubility of this compound. Compound (IV) gave better exhaustion.

TABLE 2 Dyebath Exhaustion of Compound (III) and Compound (IV)

Application Level (%wool weight)	Dyebath Concentration (mg/L)	Loss in Liquors (%)	Wool Analysis (mg/kg wool)	Recovery on wool (%)
Cmpd(III)(0.001)*	0.21	53		
Cmpd (III) (0.002)	0.45	56		
Cmpd.(III)(0.005)	1.28	64		
Cmpd.(III)(0.01)	2.64	66	47(0.0047)*	47
Cmpd(III)(0.02)	5.35	67	93(0.0093)	47
Cmpd(IV) (0.001)	0.16	43	7.2(0.00072)	72
Cmpd. (IV) (0.002)	0.26	33	12(0.0012)	60
Cmpd. (IV) (0.005)	0.60	30	33(0.0030)	66
Cmpd. (IV) (0.01)	1.20	30	57(0.0057)	57
Cmpd. (IV) (0.02)	2.3	29	125(0.0125)	63
Cmpd. (IV) (0.05)	2.9	15		

* Bracketed values are concentration of compounds on wool expressed as % weight on wool.

Exhaustion of Compound (IV) followed a Freundlich absorption isotherm (Fig 1) with slope near unity, indicating that concentration in the wool was proportional to the concentration in the liquor. Losses will therefore be dependent on the liquor:wool ratio

used in the dyeing, and percentage losses will be smaller at liquor ratios shorter than the 25:1 used in this initial work. Levels in rinse liquors are very low, indicating good penetration of the fibre, and hydrolysis and volatility losses are low as indicated by the good overall recoveries of the active ingredient in wool and liquors.

Durability Requirements of Mothproofing Chemicals

Insect-resist activity is required to persist through the life-time of a wool product. Application of a 5-10 fold excess of active ingredient above the minimum active level ensures insect protection even after 80-90% losses through volatility, exposure to light, and cleaning (washing, shampooing and drycleaning).

Light Fastness and Volatility

Light stability and long-term volatility are the main factors in deciding durability of an insect-resist treatment over the anticipated life time of 20 years that can reasonable be expected from a domestic carpet. Volatility losses are an integral part of light fastness testing because high temperatures may be reached in exposure testing. Experience with permethrin has shown that it may be lost from the surface of fabric with a half-life of 12 days at 60°C if it is applied under conditions where it does no penetrate the fibre, but it can 'permanently' protect wool when applied from high temperature dyebaths.

Compound (IV) treated fabrics were subjected to accelerated light exposure testing to exceed blue scale fastness rating 6, by which stage the fabrics were significantly yellowed and were becoming weakened. Losses were monitored by insect bioassay (Table 3) and chemical assay (Table 4, Fig 2).

TABLE 3 Insect Bioassay of Fabrics Treated with Compound (IV) after Accelerated Light Exposure Testing

Nominal Application (% on wool weight)	*Tineola* Bioassay Results* Feeding Damage (mg)				
	Light Exposure Time				
	No exposure	1 Week	2 Week	3 Week	4 Week**
0.005	4	3	3	5	6
0.002	4	6	3	7	8
0.001***	7	2,11	3,16	6,14	3,11

* Control wool fabric feeding damage 30-78mg.

** Exposures of 1, 2, 3, and 4 weeks correspond to blue scale ratings of 3, 5, and 6 respectively.

*** Duplicate sets gave variable feeding damage; both sets reported.

TABLE 4 Chemical Analysis of Compound (IV) Treated Wools after Accelerated Light Exposure

Nominal Application (% on wool weight)	Wool Analysis (Compound (IV) mg/kg wool)				
	Light Exposure Time				
	No Exposure	1 Week	2 Week	3 Week	4 Week
0.001	7.2 (100)*	5.4 (75)	4.6 (64)	4.1 (57)	4.0 (56)
0.002	12 (100)	11 (92)	8.9 (75)	8.0 (67)	7.8 (66)
0.005	33 (100)	30 (90)	26 (77)	23 (70)	23 (70)
0.01	157 (100)	54 (94)	48 (84)	44 (77)	44 (76)
0.02	125 (100)	109 (87)	96 (77)	86 (68)	84 (67)

* Bracketed values in the body of the table are percentages of the initial application remaining after the specified exposure.

Compound (IV) has more than adequated light fastness for a commercial insect-resist treatment. Under these same accelerated testing conditions, only 40-50% of an initial application of permethrin would remain.

Drycleaning and Wash Fastness

In comparison with the synthetic pyrethroid mothproofing compounds, Compound (IV) has similar washing performance and better drycleaning resistance. Losses in

handwashing are confirmed by both insect bioassay (Table 5) and by chemical analysis (Table 6, and Fig. 3). Losses in drycleaning are small (Table 6, Fig. 4).

TABLE 5 Insect Bioassay of treated fabrics after Washing and Drycleaning

Compound	Nominal Application (% on wool weight)	*Tineola* Bioassay Results Feeding Damage (mg)				
		As Treated	Hand Washing		Drycleaning	
			5 Cycles	10 Cycles	5 Cycles	10 Cycles
Compd. (III)*		4	9	58		
	0.1	7	13	90		
	0.05	8	26	97		
	0.025					
Cmpd. (IV)**	0.005	4	7	5	3	3
	0.002	4	17	20	9	6
	0.001	7	30	44	9	7

* Control wool fabric feeding damage 109-140mg.

** Control wool fabric feeding damage 48-65mg.

TABLE 6 Chemical Analysis of Compound (IV) Treated Wools after Drycleaning and Washing.

Nominal Application (% on wool weight)	Wool Analysis (%Cmpd. (IV) oww)				
	As Treated	Hand Washing		Drycleaning	
		5 Cycles	10 Cycles	5 Cycles	10 Cycles
0.001	7 (100)	2.2 (30)*	1.5 (20)		
0.002	12 (100)	4.8 (40)	2.8 (23)	12 (102)	10 (85)
0.005	33 (100)	13 (40)	6.6 (20)	29 (88)	29 (86)
0.01	57 (100)	24 (43)	16 (27)	58 (102)	54 (95)
0.02	125 (100)	55 (44)	29 (23)	119 (95)	120 (96)

* Bracketed values in the body of the table are percentages of the initial amount remaining after the specified exposure.

Dry cleaning is a severe test for the non-polar pyrethroids (permethrin or cycloprothrin) and 70% of an initial application would be removed after 5 commercial dry-cleaning treatments. Compound (IV) was largely unchanged. After 5 hand washing cycles, 45% of applied pyrethroid remained on the wool, and Compound (IV) showed similar performance. For the main end-use of carpeting, the most important wet treatment is carpet shampooing; losses of 30% after 5 cycles are usual for the pyrethroids, and Compound (IV) should behave similarly. These factors are important in deciding the ultimate application rate for each material. In practice, compound Compound (IV) may

need to be applied at around 0.005-0.01% active ingredient to compensate for losses in application, light and wet treatments such as carpet shampooing.

Compositions containing Compounds active against Beetles

Permethrin Results:

SET 1: *Tinea translucens* (long term test)

%Cmpd. (IV) owf	0	0.0025	0.0050	0.0075	0.010
feeding damage(mg)	200	21	1	1.5	1

(owf=on weight of fabric)

SET 2: *Anthrenus flavipes* (2 week test)

%Cmpd. (IV) owf	0	0.001	0.0025	0.005	0.0075	0.01
%permethrin owf	0	0	0	0	0	0
feeding damage(mg)	81,125	71,20	100,71	106,138	94,56	52,20

SET 3: *Anthrenus flavipes* (2 week test)

%Cmpd. (IV) owf	0	0.001	0.0025	0.005	0.0075	0.01
%permethrin owf	0.003	0.003	0.003	0.003	0.003	0.003
feeding damage	17,15	9,13	9,5	5,18	10,15	2,5

These results clearly show that Compound (IV) has high activity against moths (set 1), but no activity agains beetles (set 2) except at the highest level in the concentration range studied. The presence of Compound (IV) does however, increase the activity of the permethrin (ie leads to lower feeding damage) from the comparison with damage of a permethrin-only treatment (15,17mg for duplicate samples). The effect roughly corresponds to a doubling in activity.

As an example there may again be a synergistic effect with the HHP derivative, as the Compound (IV) improves its activity:

HHP derivative Results:

SET 4: *Anthrenus flavipes* (2 week test)

%Cmpd. (IV) owf	0	0	0.006	0	0.006
%HHP owf feeding	0	0.01	0.01	0.02	0.02
Feeding Damage (mg)	108	7.7	4.1	2.5	1.9

SET 5: pyrethroid-resistant *Tinea translucens* (4 week test)

Bifenthrin on wool (mg/kg)	0	6	10	20	30
Feeding Damage	41	38	41	44	37

(Conclusion: Bifenthrin is inactive at 0.003% on wool weight against pyrethroid resistant clothes moths)

SET 6: pyrethroid-susceptible *Tinea translucens* (2 week test)

Bifenthrin on wool (mg/kg)	0	1	2	3	4
Feeding Damage (mg)	31	12	4	4	4

(Conclusion: Bifenthrin is active at 0.0002% on wool weight pyrethroid susceptible clothes moths)

SET 7: Beetles (*Anthrenus flavipes*) (2 week test)

Bifenthrin on wool (mg/kg)	0	1	2	3	4	5
Feeding Damage (mg)	55	15	2	4	1	1

(Conclusion: Bifenthrin is active at 0.0002% on wool weight against carpet beetles).

The results sets 1, 5 and 7 indicate that a mixture of compound IV and Bifenthrin will control pyrethroid resistant clothes moths.

SET 8: Beetles (*Anthrenus flavipes*) (2 week test)

% Compound (IV) owf	0	0	0.01
% Butyl ester of 4-hydroxybenzoic acids owf	0	0.25	0.25
Feeding Damage (mg)	28	18	3

Although Compound (IV) has little direct beetle activity at this treatment level, it greatly enhances the effect of the 4-hydroxybenzoic acid ester.

References:

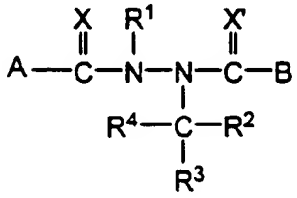
1. Australian Standard AS 2001.6.1 (1980)

2. R.J. Mayfield and I.M. Russell. J. Text. Inst., 70, 53 (1979)

It will be clear to the reader that various modifications may be made to the particular embodiments described above without departing from the spirit and scope of the present invention.

CLAIMS:

1. A method of mothproofing wool or a wool-containing product the method including treating the wool or wool-containing product with an effective amount of a compound according to formula (I):



wherein X and X' are the same or different O, S or NR;

R^1 is hydrogen; (C_1-C_6) alkyl; (C_1-C_6) alkoxy-(C_1-C_6) alkoxy-(C_1-C_6) alkyl having independently the stated number of carbon atoms in each alkyl group; (C_1-C_6) alkylthio-(C-C_6) alkyl having independently the stated number of carbon atoms in each alkyl group; (C_2-C_6) alkenyl; (C_2-C_6) alkynyl; or phen-(C_1-C_4) alkyl where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo-(C_1-C_4) alkyl (C_1-C_4)-alkoxy, halo-(C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy- carbonyl, (C_1-C_4) alkanoyloxy or NZZ';

R^2 and R^3 are the same or different hydrogen or (C_1-C_4) alkyl;

R is (C_1-C_4) alkyl substituted with 1 to 4 fluoro; straight chain (C_2-C_4) alkenyl; carboxyl; (C_1-C_3) alkoxy-carbonyl; cyano; cyano substituted (C_1-C_4) alkyl, tri(C_1-C_4)-alkysilyl having independently the stated number of carbon atoms in each alkyl group; or tri(C_1-C_2) alkylsilylmethyl having independently the stated number of carbon atoms in each alkyl group; provided that R^2 and R^3 are both alkyl when R^4 is corboxyl or alkoxycarbonyl; and

A and B are the same of different unsubstituted or substituted naphthytyl where the substituents can be from one to three of the same or different halo; nitro; (C_1-C_4)-alkoxy; (C_1-C_4) alkyl or NZZ';

unsubstituted or substituted phenyl where the substituents can be from one to five of the same or different halo; nitroso; nitro; cyano; hydroxy; (C_1-C_6) alkyl; halo-(C_1-C_6)-alkyl; cyano-(C_1-C_6) alkyl; hydroxy-(C_1-C_6)-alkyl; (C_1-C_6)alkoxy; halo-(C_1-C_6) alkoxy; (C_1-C_6) alkoxy-(C_1-C_6) alkyl having independently the stated number of carbon atoms in each alkyl group; (C_1-C_6) alkoxy-(C_1-C_6) alkoxy having independently the stated number of carbon atoms in each alkyl group; -ORSR' group; -OCO_2R group; -OCO_2H group; (C_1-$_6$) alkanoyloxy-(C_1-C_6) alkyl having independently the stated number of carbon atoms in each alkyl group; (C_2-C_6) alkenyl optionally substituted with halo, cyano, (C_1-C_4) alkyl, halo-(C_1-C_4)-alkoxy, (C_1-C_4) alkylthio or (C_1-C_4)alkoxy; (C_1-C_4)alkadienyl; (C_2-C_6) alkenyloxy; (C_2-C_6) alkenyl-carbonyl; (C_2C_6)-alkenyloxy-carbonyloxy; (C_2-C_6) alkynyl optionally substituted with halo, cyano, nitro, hydroxy, (C_1-C_4) alkoxy, halo-(C_1-C_4)alkyl, (C_1-C_4) alkylthio or (C_1-C_4)-alkyl; carboxy; -RCO_2R' group; -COR; -COH; halo-(C_1-C_6) alkyl-carbonyl; -CO_2R group; (C_1-C_6) haloalkoxy-carbonyl; -OCOR group; -$ORCO_2$R' group; amino (-NZZ'); amino substituted with hydroxy, (C_1-C_4) alkoxy or (C_1-C_4) alkylthio; -CONZZ' group; (C_2-C_6)- alkenyl-carbonylamino; hydroxy-(C_1-C_6)-alkylamino-carbonyl; -OCONZZ' group; -NZCOZ' group; -$NZCO_2$Z' group; thiocyanato; isothiocyanato; (C_1-C_6) thiocyanatoalkyl; (C_1-C_6) alkylthio; halo-(C_1-C_6) alkylthio; -S(O)Z group; -SO_2Z group; -OSO_2R group; -OSO_2H group; -SO_2NZZ' group; -CSR group; -CSH group; -SCOR group; -SCOH group -NSCSZ' group; unsubstituted or substituted phenyl having one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, amino, (C_1-C_4)-alkylamino or di(C_1-C_4) alkylamino having independently the stated number of carbon atoms in each alkyl group; phenoxy where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo-(C_1-C_4) alkyl, (C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkyl-carbonyl, (C_1-C_4)alkanoyloxy, amino, (C_1-C_4)-alkylamino or di(C_1-C_4)alkylamino having independently the stated number of carbon atoms in each alkyl group; benzoyl where the phenyl ring is unsubstituted or substituted with one to three of the same or different

halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, amino, (C_1-C_4) alkylamino or di(C_1-C_4)alkylamino having independently the stated number of carbon atoms in each alkyl group; benzoyloxy (C_1-C_6)alkyl; phenylthio-(C_1-C_6) alkyl where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy,(C_1-C_4) alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)-alkanoyloxy, amino, (C_1-C_4)alkylamino or di(C_1-C_4)alkylamino having independently the stated number of carbon atoms in each alkyl group; -CR=N-R'" group where R'" is hydroxy, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, amino (-NZZ'), phenylamino, -COR, -COH or benzoyl; (C_2-C_6) oxiranyl; acetylthiosemi- carbazone; pyrrolyl; oxazolyl, unsubstituted or substituted with one or two methyl group; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups may be joined to form, together with the carbon atoms to which they are attached, a 5 or 6 membered dioxolano or dioxano heterocyclic ring; unsubstituted or substituted (C_1-C_{10})alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkoxy, halo-(C_1-C_4)alkoxy, carboxy, (C_1C_4)-alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, phenyl or -NZZ';

unsubstituted or substituted (C_3-C_8) cycloalkyl or unsubstituted or substituted (C_3-C_8) cyclo (C_1-C_4) alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alyl, halo-(C_1-C_4)-alkyl, (C_1-C_4) alkoxy, halo-(C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkanoyl, (C_1-C_4)-alkoxy-carbonyl, (C_1-C_4) alkanoyloxy or -NZZ';

unsubstituted or substituted (C_2-C_8)alkenyl or unsubstituted or substituted (C_2-C_8)-alkadienyl having as substituent(s) a furyl, thienyl or pyridyl or one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, (C_3-C_6)cycloalkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-(C_1-C_4)alkoxy, carboxy, (C_1-C_4)-alkoxyl-carbonyl, (C_1-C_4) alkanoyloxy or -NZZ';

unsubstituted or substituted (C_3-C_8)cycloalkenyl or unsubstituted or substituted (C_3-C_8)cycloalkadienyl having as substituent(s) one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)-alkoxy, halo-(C_1-C_4)alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy or -NZZ';

unsubstituted or substituted (C_2-C_8)alkynyl having as substituent(s) one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-(C_1-C_4)alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, phenyl or -NZZ';

phenalkyl having one to four carbon atoms in the alkyl group and wherein the alkyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C_1-C_4)alkoxy, (C_1-C_4)-alkoxy-carbonyl or -NZZ' and the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, halo-(C_1-C_4)alkyl, cyano-(C_1-C_4)alkyl, (C_1-C_4)-alkoxy, halo-(C_1-C_4) alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, (C_2-C_6)alkenyl, halo-(C_2-C_6)alkenyl, (C_2-C_6)alkynyl or -NZZ';

phenalkenyl having two to six carbon atoms in the alkenyl group and the alkenyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C_1-C_4)alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-(C_1-C_4)alkoxy, (C_1-C_4)-alkoxy-carbonyl or -NZZ', and the phenyl ring is unsubstituted or substituted with one to or three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-(C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy or -NZZ';

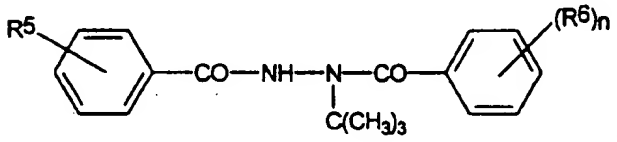
unsubstituted or substituted five-membered heterocycle selected from furyl, thienyl, triazolyl, pyrrolyl, isopyrrolyl, pyrazolyl, isoimdazolyl, thizolyl, isothiazolyl, oxazolyl and isooxazolyl where the substituents can be from one to three of the same or different halo; nitro; hydroxy; (C_1-C_6)alkyl; (C_1-C_6)alkoxy; carboxy; (C_1-C_6) alkoxy-carbonyl; -RCO_2H group RCO_2R' group; -CONZZ' group; amino (-NZZ'); -NZCOZ' group; (C_1-C_6)alkylthio; or unsubstituted or halo substituted phenyl having one to three of the same or differnt halo, nitro, (C_1-C_6)alkyl, halo-alkyl, (C_1-C_6)alkoxy, halo- (C_1-C_6)-alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl or amino (-NZZ'); or

unsubstituted or substituted six-membered heterocycle having one, two, three or four nitrogen atoms and two to five nuclear carbon atoms where the substituents can be from one to three of the same or different halo; nitro; hydroxy; (C_1-C_6)alkyl; (C_1-C_6)alkoxy; carboxy; (C_1-C_6)-alkoxy-carbonyl; -RCO_2H group; -RCO_2R' group; -CONZZ' group; amino (-NZZ'); -NZCOZ' group; (C_1-C_6)alkylthio; or unsubstituted or substituted

phenyl having one to three of the same or different halo, nitro, (C_1-C_6)alkyl, halo-(C_1-C_6)alkyl, (C_1-C_6) alkyl, (C_1-C_6)alkoxy, halo-(C_1-C_6)- alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl or amino (-NZZ');

where R and R' are (C_1-C_6)alkyl; Z and Z' are hydrogen or (C_1-C_4)alkyl; "amino" means NZZ'.

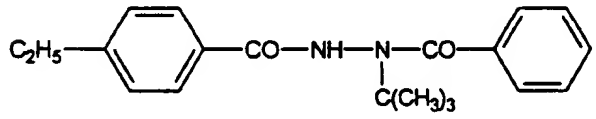
2. A method according to claim 1 wherein the treatment compound is a compound of formula (II)



(II)

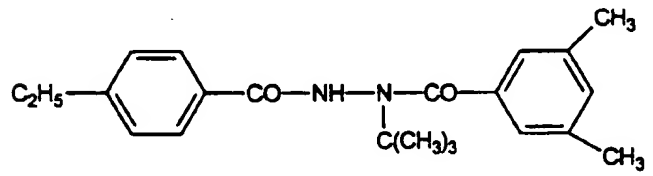
where R^5 and R^6 may be the same or different and may be H or C_{1-3} alkyl and may be 1-6.

3. A method according to claim 2 wherein the treatment compound is a compound formula (III)



(III)

4. A method according to claim 2 wherein the treatment compound is a compound of formula (IV)



(IV)

5. A method according to any one of the preceding claims wherein the treatment compound is applied at a level of about 0.001%-0.5% based on the wool weight.

6. A method according to any one of the preceding claims wherein treatment compound is applied as a solution in an organic solvent.

7. A method according to any one of claims 1 to 5 wherein the treatment compound is applied as a suspension, self-emulsifiable concentrate or other water-based formulation.

8. A method according to any one of the preceding claims wherein the treatment compound is applied in a dyebath, by continuous padding or in a scouring application.

9. A method according to any one of the preceding claims wherein the treatment compound is applied at 5-10 fold excess of the minimum active level of the treatment compound.

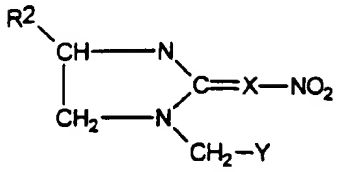
10. A method according to any one of the preceding claims wherein the wool or wool-containing product is also treated with an agent having an activity against beetles.

11. A method according to claim 10 wherein the agent active against beetles is selected from the group natural or synthetic pyrethroids, repellants and disinfectants, and insect resist agents of the aryl ureido and amide classes.

12. A method according to claim 11 wherein the beetle agent is selected from permethrin or bifenthrin.

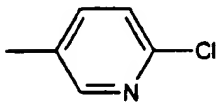
13. A method according to claim 11 wherein the beetle agent is selected from the group N-(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-6-hydroxy-1,3-dimethyl-2,4-dioxo-5-pyrimidine carboxamide or N,N'-bis[4-chloro-3-(trifluoromethyl)phenyl] urea, butyl ester of 4-hydroxybenzoic acid and 5-chloro-2-(4-chloro-2-(3,4-chlorophenyl))phenoxyureido benzene sulphonate or alkali salt thereof.

14. A method according to claim 10 wherein the beetle agent is a compound of formula (V)



(V)

where R^2 is H or CH_3; X is CH or N; and Y is



15. A method according to any one of claims 10 to 14 wherein the beetle agent is applied at a level of about 0.0001% to 0.1%.

16. A method according to any one of claims 10 to 15 wherein the treatment compound is applied simultaneously with the beetle agent.

17. A treatment composition containing a treatment compound according to any one of claims 1 to 5.

18. A treatment composition according to claim 17 further including an agent having activity against beetles.

19. A treatment composition according to any one of claims 16 and 17 in the form of a dye bath composition.

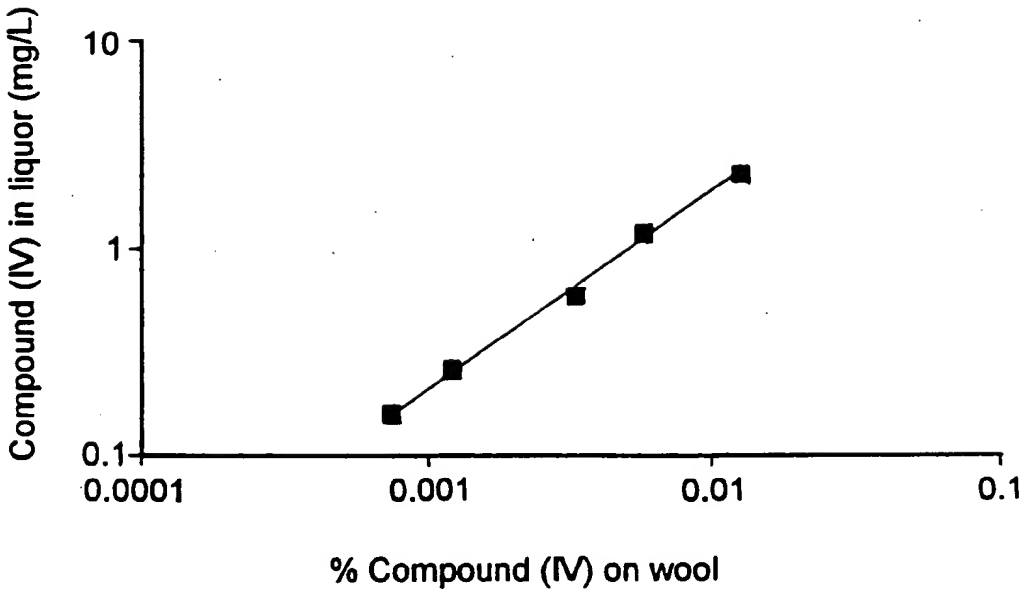

Compound (IV) in liquor (mg/L)
10
1
0.1
0.0001
0.001
0.01
0.1
% Compound (IV) on wool

FIG 1

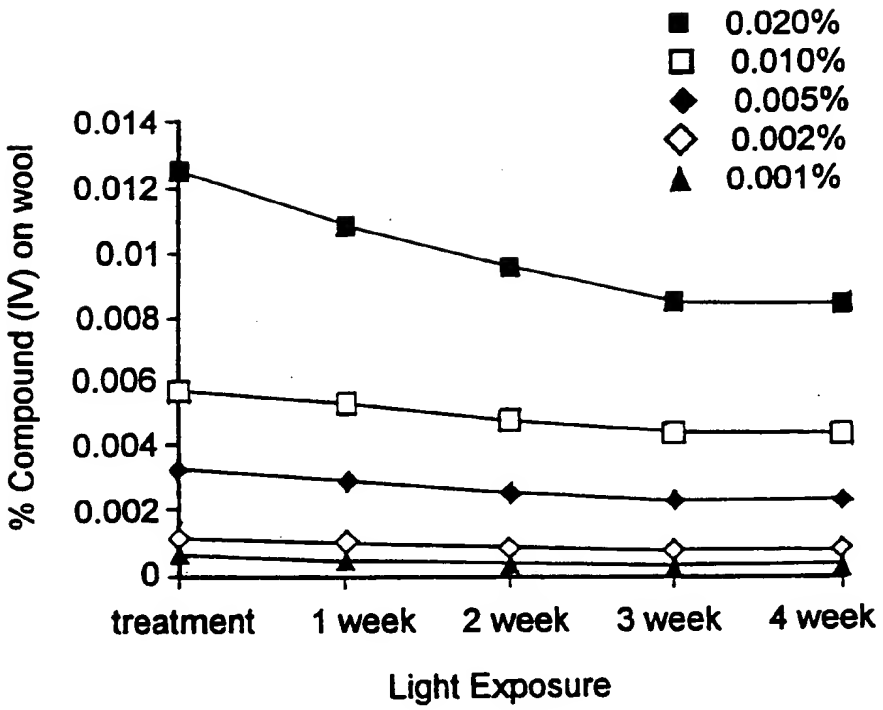

0.020%
0.010%
0.005%
0.002%
0.001%
% Compound (IV) on wool
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
treatment
1 week
2 week
3 week
4 week
Light Exposure

FIG 2

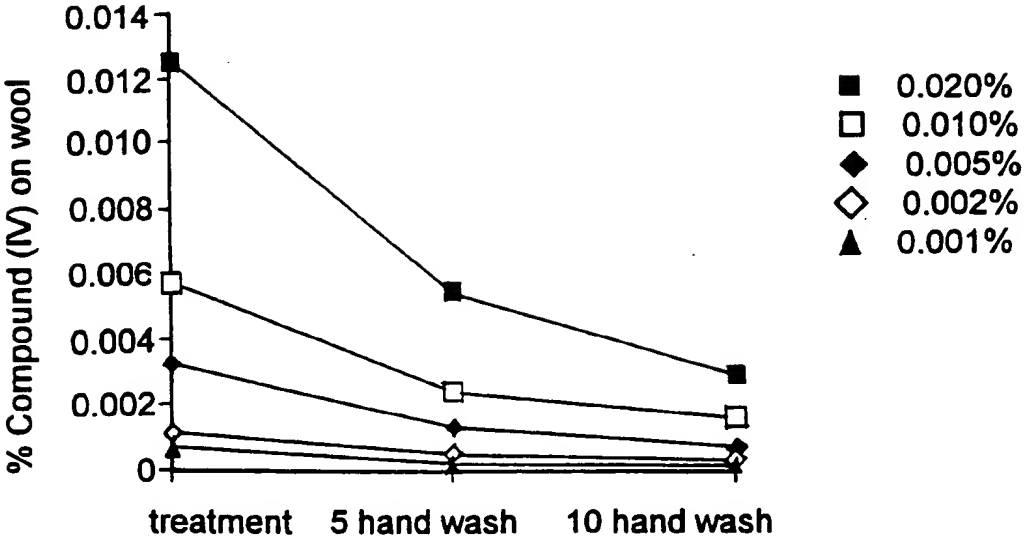

0.014
0.012
0.010
0.008
0.006
0.004
0.002
0
% Compound (IV) on wool
treatment
5 hand wash
10 hand wash
0.020%
0.010%
0.005%
0.002%
0.001%

FIG 3

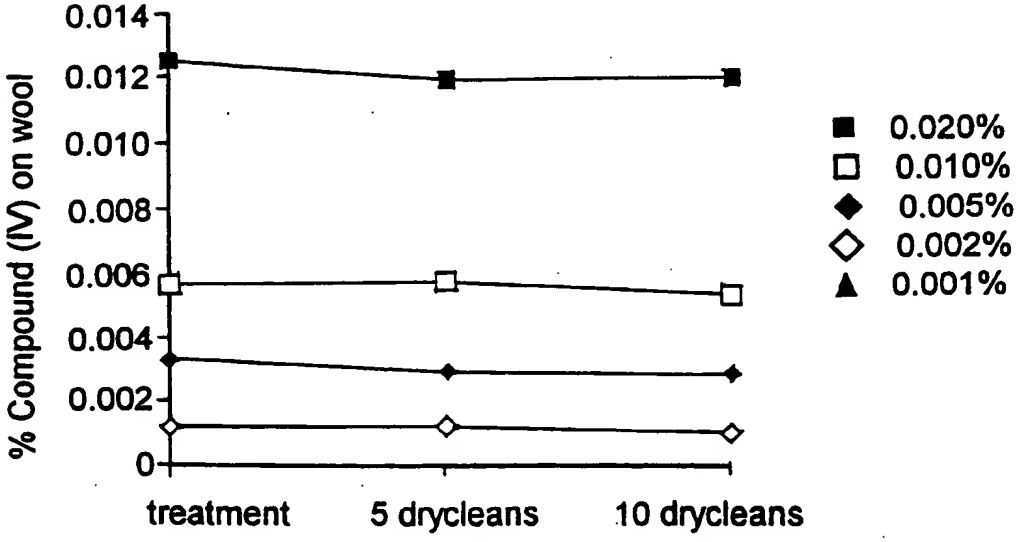

0.014
0.012
0.010
0.008
0.006
0.004
0.002
0
% Compound (IV) on wool
treatment
5 drycleans
10 drycleans
0.020%
0.010%
0.005%
0.002%
0.001%

FIG 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 94/00527

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl.[6] A01N 37/28, 37/52, 55/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int. Cl. A01N 37/28, 37/52

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
DERWENT
JAPIO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	AU,B, 76287/87 (599124) (ROHM AND HAAS COMPANY) 20 October 1988 (20.10.88) whole document	1-13, 15-19
X	AU,B, 71473/87 (595303) (ROHM AND HAAS COMPANY) 4 February 1988 (04.02.88) whole document	1-13, 15-19
X	AU,B, 71472/87 (599970) (ROHM AND HAAS COMPANY) 31 March 1988 (31.03.88) whole document	1-13, 15-19

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 November 1994 (02.11.94)	10 Nov 1994 (10.11.94)
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929	Authorized officer GJ McPeice for STEVE CHEW Telephone No. (06) 2832248

Form PCT/ISA/210 (continuation of first sheet (2)) (July 1992) cophin

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X	AU,B, 71471/87 (602516) (ROHM AND HAAS COMPANY) 5 November 1987 (05.11.87) whole document	1-13, 15-19
X	AU,A, 69266/87 (ROHM AND HAAS COMPANY) 3 September 1987 (03.09.87) whole document	1-13, 15-19
X	AU,A, 67894/87 (ROHM AND HAAS COMPANY) 23 July 1987 (23.07.87) whole document	1-13, 15-19
X	AU,B, 64289/86 (595912) (ROHM AND HAAS COMPANY) 30 April 1987 (30.04.87) whole document	1-13, 15-19
X	AU,A, 36454/89 (ROHM AND HAAS COMPANY) 21 December 1989 (21.12.89) whole document	1-13, 15-19
X	GB,A, 2231268 (ROHM AND HAAS COMPANY) 14 November 1990 (14.11.90) whole document	1-13, 15-19

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
AU	76287/87	AT	61044	DE	3768264	EP	286746
		GR	3001522	HU	202719	PT	84965
		TR	23597	CA	1273633	JP	63267752
		ZA	8702740	IL	82266	PT	84965
		DK	169321				
AU	81471/87	AT	77200	BR	8701825	CA	1281716
		DE	3779814	EG	18437	EP	245950
		ES	2042556	IL	82242	JP	62263150
		ZA	8702519	US	5225443	US	5117057
AU	71472/87	AT	83481	BR	8701822	CA	1331189
		DE	3783111	DK	1994/87	EG	18453
		EP	261755	ES	2053535	HU	202830
		IL	82244	JP	63083063	PT	84718
		TR	23373	ZA	8702738		
AU	71473/87	AT	69220	BR	8701820	CA	1310641
		DE	3774347	DK	165961	EG	18544
		EP	253468	ES	2037709	GR	3003079
		HU	202831	IL	82278	JP	63023866
		TR	23319	ZA	8702664	US	5354762
AU	67894/87	BR	8700246	DE	3768515	EG	18196
		EP	232075	ES	2037076	GR	3001621
		IL	81360	JP	62209053	KR	9100856
		TR	23119	ZA	8700430		
AU	69266/87	AT	62474	BR	8700931	CA	1295618
		DE	3769172	EG	18279	EP	234944
		ES	2032818	GR	3001945	IL	81706
		JP	62234055	TR	23120	ZA	8701432
AU	36454/89	AT	93839	BR	8902892	CN	1040191
		DE	68908789	DK	2914/89	EG	18874
		EP	347216	IL	90606	JP	2042049
		NZ	229536	PT	90863	ZA	8904510
AU	64289/86	AT	60979	BR	8605121	CA	1281332
		DE	3677761	DK	4835/86	EG	18034
		EP	236618	ES	2033235	GR	3001519
		HU	205535	IL	80369	JP	62167747
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		US	4985461	ZA	8607921		
GB	2231268	NZ	228936	SG	345/93		

END OF ANNEX